STUDIES ON THE MECHANISM OF THE CONJUGATE ADDITION OF GRIGNARD REAGENTS

BY

GEORGE ROBERT CORAOR

A.B., Illinois College, 1947
A.M., University of Illinois, 1948

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1950

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STUDIES ON THE MECHANISM OF THE CONJUGATE ADDITION OF GRIGNARD REAGENTS

Introduction

The mechanism of the conjugate addition of Grignard reagents to α,β-unsaturated ketones has not been established. It has been suggested,[1] however, that the reaction proceeds by the preliminary coordination of the carbonyl oxygen atom with the magnesium atom of the Grignard reagent followed by the intramolecular transfer of the R group to the β-carbon atom of the ketone through a cyclic transition state complex. It was the purpose of this investigation to determine the validity of this proposal.

In five and six-membered cyclic, unsaturated ketones, the β-carbon atom is held in such a position that the formation of a cyclic intermediate is impossible. Since several of these cyclic ketones have been observed to undergo some 1,4 addition,[2] the mechanism in question cannot be the only one by which conjugate addition occurs. If it is one of two or more mechanisms which result in conjugate addition, such linear ketones as 3-hexen-2-one, which are capable of forming the cyclic intermediate should exhibit more 1,4 addition than those which are incapable of doing so.

Therefore, a comparison was made of the amount of conjugate addition to analogous pairs of cyclic and linear ketones such as 2-cyclohexen-1-one and 3-hexen-2-one.

Discussion of Results

3-Penten-2-one, 3-hexen-2-one, 3-hepten-2-one, 4-hexen-3-one and 2-cyclohexen-1-one were prepared and allowed to react with ethylmagnesium bromide, *iso*-propylmagnesium bromide and *t*-butylmagnesium chloride. The amount of conjugate addition each ketone underwent was determined by first showing that no starting material was present and then by

analyzing the reaction product for the presence of carbonyl compounds by the method of Bryant and Smith.[3]

The per cent conjugate addition observed for these ketones is listed below in the order of ethylmagnesium bromide, *iso*-propylmagnesium bromide and *t*-butylmagnesium chloride: 3-penten-2-one: 52, 65, 61; 3-hexen-2-one: 43, 56, 48; 3-hepten-2-one: 51, 63, 60; 4-hexen-3-one: 68, 80, 66 and 2-cyclohexen-1-one: 23, 65, 62.

Benzalpropiophenone and 2-methylinden-1-one were also prepared and the amounts of conjugate addition of ethylmagnesium bromide to each determined. Benzalpropiophenone was observed to yield only the conjugate addition product, whereas 2-methylinden-1-one underwent approximately 25% 1,4 addition.

These data indicate that the cyclic mechanism is not the only one by which conjugate addition occurs and furthermore that the cyclic mechanism can account for only a small part of the 1,4 addition which the unsaturated compounds examined were found to undergo.

BIBLIOGRAPHY

1. Johnson, Gilman, "Organic Chemistry", John Wiley and Sons, New York, 1947, Ed. 2, Vol. 2, pp. 1881-2.
2. Whitmore and Pedlow, J. Am. Chem. Soc., 63, 758-60 (1941)
3. Bryant and Smith, J. Am. Chem. Soc., 57, 1326 (1935)

VITA

The author was born in Jacksonville, Illinois, on May 10, 1924. He attended the public schools of that city and was graduated from the Jacksonville High School in June, 1942. After attending Illinois College for one year, he served in the United States Navy from July, 1943 to June, 1946. He then returned to Illinois College, from which he was graduated in June, 1947 with the degree of Bachelor of Arts. In September, 1947, he entered the Graduate College of the University of Illinois, where he held a third-year University Fellowship. In 1948 he received the degree of Master of Arts from that institution.

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